

**CH₄ and N₂O
exchange over
a managed hay
meadow**

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G. Wohlfahrt

Methane and nitrous oxide exchange over a managed hay meadow

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Abstract

The methane (CH₄) and nitrous oxide (N₂O) exchange of a temperate mountain grassland near Neustift, Austria, was measured during 2010–2012 over a time period of 22 months using the eddy covariance method. Exchange rates of both compounds at the site were low, with more than 95 % of the half-hourly fluxes of CH₄ and N₂O ranging between ±10 and ±1 nmol m⁻² s⁻¹, respectively. The meadow acted as a sink for both compounds during certain time periods, but was a clear source of CH₄ and N₂O on an annual time scale. Therefore, both gases contributed to an increase of the global warming potential (GWP), effectively reducing the sink strength in terms of CO₂-equivalents of the investigated grassland site. In 2011, our best guess estimate showed a net GHG sink of -32 g CO₂-equ. m⁻² yr⁻¹ for the meadow, whereby 55 % of the CO₂ sink strength of -71 g CO₂ m⁻² yr⁻¹ was offset by CH₄/N₂O emissions of 7/32 g CO₂-equ. m⁻² yr⁻¹. When all data were pooled, the ancillary parameters explained 26/38 % of observed CH₄/N₂O flux variability, and up to 62/75 % on shorter time scales in-between management dates. In case of N₂O fluxes, we found highest emissions at intermediate soil water contents and at soil temperatures close to zero or above 14 °C.

In comparison to CO₂, H₂O and energy fluxes, the interpretation of CH₄ and N₂O exchange was challenging due to footprint heterogeneity regarding their sources and sinks, uncertainties regarding post-processing and quality control. Our results emphasize that CH₄ and N₂O fluxes over supposedly well-aerated and moderately fertilized soils cannot be neglected when evaluating the GHG impact of temperate managed grasslands.

1 Introduction

Methane (CH₄) and nitrous oxide (N₂O) are the most important anthropogenic greenhouse gases (GHG) after carbon dioxide (CO₂). Due to their long atmospheric lifetimes of approx. 9 and 131 years (Prather et al., 2012), respectively, both compounds are

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well-mixed in the atmosphere and can influence atmospheric chemistry directly and indirectly. The emission or deposition strength of terrestrial ecosystems is possibly influenced by climate change, which may trigger important feedbacks to the global climate system (Xu-Ri et al., 2012). CH₄ and N₂O could be important agents in GHG mitigation strategies for managed grasslands due to their emission from agriculture, mainly as a consequence of land use change, management events and animal husbandry. In order to assess the effectiveness and feasibility of such mitigation strategies, long-term year-round GHG measurements are indispensable. Both compounds are characterized by high spatial and temporal variability of their respective fluxes (Baldocchi et al., 2012; Imer et al., 2013).

Methane has a major influence on climate and chemistry of the atmosphere (Crutzen and Lelieveld, 2001; Khalil et al., 2007). CH₄ can react with hydroxyl radicals, resulting in a reduction of the oxidizing capacity of the atmosphere and the production of ozone (O₃) in the troposphere. Methane can influence the lifetime or production of other atmospheric constituents like stratospheric water vapor and CO₂ (Boucher et al., 2009; Collins et al., 2010; Shindell et al., 2009). Its global warming potential over a 100 year lifespan (GWP) and on a per molecule basis is 25 times that of CO₂ (Forster et al., 2007) or higher when the production of CO₂ from CH₄ oxidation is taken into account (Boucher et al., 2009). Atmospheric CH₄ increased significantly since the industrial revolution until the end of the 1990s, remained constant for nearly a decade and again began to increase after 2007 (Nisbet et al., 2014). This recent increase is most likely the consequence of anomalously high temperatures in the Arctic in 2007 and above-average precipitation in the tropics in 2007 and 2008 (Bousquet et al., 2011; Dlugokencky et al., 2009).

The main portion of global CH₄ originates from single-celled archaea (methanogens) found in anaerobic microsites in the soil, in water-saturated zones rich in carbon and in the digestive systems of ruminants (Baldocchi et al., 2012; Whalen, 2005). CH₄ is also emitted from organic waste deposits, e.g. manure, and from thermogenic and pyrogenic sources (Kirschke et al., 2013). Highest emissions were previously reported

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from regions with intensive agriculture and animal husbandry (Schulze et al., 2009). Generally, methane emissions by plants under aerobic conditions seem to play only a minor role in the global CH₄ budget (Kirschke et al., 2013).

The main sink of methane is through its reaction with the hydroxyl radical OH in the troposphere (Ehhalt and Heidt, 1973). Other, minor sinks are methanotrophic bacteria in aerated soils and reactions with atmospheric constituents in the stratosphere and the marine boundary layer (Allan et al., 2007; Cicerone and Oremland, 1988). Previous studies reported reduced CH₄ deposition in a forest and in a temperate grassland due to elevated CO₂ (Dubbs and Whalen, 2010; Ineson et al., 1998; Phillips et al., 2001) and increased CH₄ uptake due to warming in a temperate forest and several subarctic ecosystems (Peterjohn et al., 1994; Sjögersten and Wookey, 2002).

Nitrous oxide can deplete O₃ in the upper and increase O₃ in the lower regions of the stratosphere (Revell et al., 2012). It can therefore influence tropospheric chemistry by increasing the stratosphere–troposphere exchange of O₃ and odd nitrogen species, and by increasing OH formation (Prather and Hsu, 2010). Similar to CH₄, N₂O has a high warming potential, 298 times that of CO₂ over a 100 year lifespan (Forster et al., 2007). The dominant source of N₂O is microbial production through nitrification and denitrification processes in soils, which is fueled by accelerated use of nitrogen fertilizers in agriculture (Davidson, 2009; Fowler et al., 2009). These microorganisms are most active when nitrogen (N) is abundant, for example after the application of synthetic fertilizers or animal manure, the most concentrated forms of anthropogenic N inputs (Davidson, 2009). Pulses of N₂O emissions from soils after fertilization were described in earlier studies (Jäger et al., 2013).

The production of N₂O by bacteria in soils is controlled by a number of factors, for example soil water content, temperature and labile carbon availability (Barnard et al., 2005; Xu-Ri and Prentice, 2008). The effect of warming on N₂O exchange is inconsistent (Dijkstra et al., 2013), but previous studies reported that warming and elevated CO₂ could increase N₂O emissions from fertilized urban lawns and grasslands (Bijoor et al., 2008; Dijkstra et al., 2013; Lam et al., 2011) as well as from non-agricultural

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soils (Khalil and Rasmussen, 1989), reduce the response of N₂O flux to grazing in an alpine meadow (Hu et al., 2010) and – in combination with enhanced nitrogen supply – amplify fire effects on soil N₂O emissions (Niboyet et al., 2011). Food production was described as the largest single source of N₂O (Syakila and Kroeze, 2011). Photolysis and oxidation reactions in the stratosphere are the main processes involved in N₂O depletion (Prather et al., 2012). Agricultural soils are characterized by high N availability from fertilization and are therefore unlikely to act as a sink for N₂O (Syakila and Kroeze, 2011).

Denitrification is an anaerobic process (Zumft and Kroneck, 2007) that is likely exclusively responsible for N₂O uptake in the soil (Vieten et al., 2008). On a global scale, the uptake of N₂O by soils may be limited (Chapuis-Lardy et al., 2007). Schlesinger (2013) estimated that the global N₂O sink in soils is not more than 2% of current estimated sources in the atmosphere. Deposition fluxes to the soil were reported before, e.g. for grasslands, forests, low-nitrogen soils, wetlands and peatlands (Dijkstra et al., 2013; Flechard et al., 2005; Goldberg and Gebauer, 2009a, b; Schlesinger, 2013; Syakila et al., 2010; Wu et al., 2013).

In this work we present long term eddy covariance CH₄ and N₂O fluxes above a temperate mountain grassland near Neustift, Austria. To this end we investigated 22 months of diurnal, seasonal and interannual exchange rates of both compounds at ecosystem scale and in relation to biotic and abiotic drivers under in situ conditions. The objective of this study is to compare our findings to previous results from chamber and eddy covariance measurements at ecosystem scale and from laboratory measurements.

Based on earlier studies we hypothesized for both compounds that (1) the investigated grassland, due to generally well-aerated soils and modest fertilizer input, is characterized by low fluxes and (2) exchange patterns are predominantly driven by soil parameters. In addition we assumed that (3) despite their low fluxes, CH₄ and N₂O exchange significantly contribute to the GHG balance of the meadow.

The study site Neustift, a managed temperate mountain grassland in Austria that is cut three times per year for hay production, was selected because it has been the focus of numerous studies over the last ten years and is therefore well described in terms of management effects, net ecosystem CO₂, H₂O, energy (Brilli et al., 2011; Hammerle et al., 2008; Wohlfahrt et al., 2008b) and VOC exchange (Bamberger et al., 2010, 2011; Brilli et al., 2012; Hörtnagl et al., 2011, 2013; Müller et al., 2010; Ruuskanen et al., 2011).

2 Methods

2.1 Site description

The study site is an intensively managed meadow in the middle of the flat valley bottom of the Stubai Valley in the Austrian Alps, in proximity of the village of Neustift (47°70' N, 11°19' E) at an elevation of 970 m a.s.l. The climate is humid continental with alpine influences, with an average annual temperature of 6.5 °C, the average annual precipitation amounts to 852 mm. The fetch is homogeneous up to 300 m to the north-northeast (the dominant daytime wind direction) and 900 m to the south-south-west (nighttime) of the instrument tower, parallel to the Valley's orientation. Typically, higher wind speeds and unstable conditions result in a smaller footprint during daytime than during nighttime, where the footprint of the site is larger due to the stable stratification of the atmosphere (Bamberger et al., 2010). The vegetation of the meadow is dominated by a few graminoids (*Dactylis glomerata*, *Festuca pratensis*, *Phleum pratensis*, *Trisetum flavescens*) and forbs (*Ranunculus acris*, *Taraxacum officinale*, *Trifolium repens*, *Trifolium pratense*, *Carum carvi*), while the slopes of the surrounding mountains are covered mainly by coniferous forest. The soil was classified as a Fluvisol (FAO classification) and is approximately 1 m deep, with a thin organic layer (0.001 m), followed by an A horizon that extends down to 0.02 m and a B horizon, best described as a sandy loam. The organic volume fraction of the A horizon is approximately 14 %.

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Measurements of CH₄ and N₂O for this work were conducted from 13 April 2010–29 February 2012 (684 days). In each year, the meadow was cut three times, with the 1st cut on 5/6 June in 2010/2011, respectively, the 2nd cut on 31 July/1 August and the 3rd cut on 20/26 September. In addition, the meadow was fertilized by manure spreading between 18–22 October 2010 and on 18 and 19 October 2011. The meadow was snow-covered from 1 January–28 February 2010, from 26 November 2010–10 March 2011 and from 7 December 2011–24 March 2012, resulting in a total of 246 snow days for this analysis. During the measurement campaign, no cows were present on the meadow.

2.2 Eddy covariance measurements

The net ecosystem exchange for CH₄ and N₂O was calculated by combining the 20 Hz three-dimensional wind speeds quantified by a sonic anemometer (R3IA, Gill Instruments, Lymington, UK) at a height of 2.5 m above ground with the simultaneously detected volume mixing ratios (VMRs) of CH₄ and N₂O, which were both measured by a commercially available continuous-wave quantum cascade laser (QCL; CWQC-TILDAS-76-D, Aerodyne, USA). Fluxes were then calculated using the virtual disjunct eddy covariance (vDEC) method proposed by Karl et al. (2002) which is based on the eddy covariance (EC) method (Baldocchi et al., 1988; McMillen, 1988). The intake tube for the QCL was mounted at 0.2 m below the sonic anemometer and displaced laterally perpendicular to the predominating wind direction in order to minimize flux loss due to vertical and longitudinal sensor separation (Massman, 2000). Sample air was drawn from the inlet through a filter (1–2 μm, PTFE) and heated (35 °C) PFA Teflon tubing (1/4" inner diameter) of 12 m length to the QCL at a flow rate of around 8 SLPM (standard liter per minute; air volume normalized to standard temperature and pressure conditions: 273 K, 1013 hPa). Sonic anemometer data were stored to the hard drive of a personal computer (PC) using the *EddyMeas* software (O. Kolle, Max Planck Institute for Biogeochemistry, Jena, Germany). More details regarding the CO₂, H₂O

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and energy flux measurements are given in Wohlfahrt et al. (2008) and Hammerle et al. (2008).

2.3 QCL setup

Ambient air was analyzed for CH₄, N₂O and H₂O at time resolutions of 10 Hz (13 March–16 August 2010), 5 Hz (16–24 August 2010) and 2 Hz (26 August 2010–29 February 2012). The QCL and associated hardware (vacuum pump and thermo cube) were housed in a climate-controlled instrument hut next to the field site. During the last five minutes of every half-hour, CH₄- and N₂O -free air and air with known, close-to-ambient, VMRs were switched into the sampling line to determine zero and span of the QCL, respectively. The QCL was operated at a pressure of 4 kPa using a built-in pressure controller and temperature of the optical bench and housing controlled to 35 °C. Fitting of absorption spectra, storing of calculated VMRs, switching of zero/calibration valves, control of pressure lock and other system controls were realized by the TDLWintel software (Aerodyne, USA) run on a PC synchronized with the main PC collecting anemometer data using the NTP software (Meinberg, Germany).

2.4 Despiking

Similar to observations by Baldocchi et al. (2012) for methane, we experienced elevated VMRs of both compounds, but especially CH₄, at night. We attributed these increased VMRs to atmospheric phenomena in the calm and stable nocturnal boundary layer rather than to elevated biogenic emissions. Therefore, VMRs of both compounds were subjected to a rigorous outlier removal routine before entering flux calculations (Fig. 1a). The despiking method in this study is based on a median filter that runs through each half-hourly VMR time series data point by data point. In comparison to the arithmetic mean, the median value of a time series is relatively insensitive to outlier values. For each 30 min period, (1) a smoothed time series of the original VMR time series was created. This was done by replacing each original data point with the median

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value of a moving time window of ± 500 values around the respective VMR value. In order to enable the calculation of median values also for data points at the start and end of the measured time series, the first and last 500 values were copied and repeated at the start and end of the smoothed time series, respectively. (2) Each data point in the smoothed time series was then subtracted from the respective measured data point, generating a time series of differences between the two data matrices. (3) When the difference exceeded the empirically determined outlier threshold of 100 ppb, the data point in the measured time series was marked as an outlier. This outlier threshold was tailored to the CH₄ variability, but worked also well for removing extreme values in the N₂O time series. (4) The arithmetic mean without these outliers was then calculated and used to (5) replace outliers in the respective half-hourly time series. As turbulent fluctuations for final flux computations are calculated using block averaging, the contribution of these substituted data points to resulting half-hourly fluxes is minor. To better account for natural variability in the time series, three different runs with varying window sizes (± 500 , 250, 150 values) and outlier thresholds (100, 80, 60 ppb) were performed for each 30 min period.

During daytime/nighttime, at least one outlier was removed in 30/66 % of half-hourly CH₄, but only in 1/1 % of all recorded N₂O VMRs.

2.5 Flux calculations

Half-hourly fluxes of CH₄ and N₂O were then calculated using the virtual disjunct eddy covariance (vDEC) method (Karl et al., 2002) as the covariance between turbulent fluctuations of the vertical wind speed and the VMRs derived from Reynolds averaging of 30 min blocks of data. The time lag between the high-resolution wind data and the disjunct QCL time series was removed using a homemade program, resulting in a subsample of the wind data corresponding to the sampling rate of the QCL. In the same step, CH₄ and N₂O fluxes were corrected for the effect of air density fluctuations and laser band-broadening following Neftel et al. (2010), using the QCL H₂O VMR. It was shown previously that flux estimates using the vDEC method are characterized

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by a larger random uncertainty compared to the true EC, but are unbiased (Hörtnagl et al., 2010). The tubing induced delay time between the wind and the QCL concentration time series was determined in a procedure comprising multiple steps. First, the correlation coefficient between the H₂O time series measured concurrently by the QCL and a closed-path infrared gas analyzer (Li-7000, LiCor, USA), the data of which were acquired together with the sonic anemometer wind data, was optimized to remove potential time differences between the two PCs caused by deviating internal clocks, effectively adjusting the starting points of the two time series. Due to generally low values of CH₄ and N₂O fluxes at our study site, the determination of lag times between the CH₄/N₂O time series and the wind data was difficult, but worked well between the QCL H₂O signal and the wind data. Therefore, secondly, the time delay between the wind components and the QCL H₂O was determined by identifying the maximum/minimum of the cross-correlation function in a time window of ± 7 s. The frequency distribution of this search revealed a peak around 2 s. Thirdly, a second time window of ± 2 s (daytime) and ± 5 s (nighttime) was then applied around this peak and used for the final lag search between the CH₄/N₂O signal and the vertical wind velocity.

Final fluxes were then calculated using the post-processing software *EdiRe* (University of Edinburgh). Frequency response corrections were applied to raw fluxes of both compounds, accounting for high-pass (block averaging, finite impulse response filter) and low-pass (lateral sensor separation, dynamic frequency response, scalar and vector path averaging, frequency response mismatch and the attenuation of concentration fluctuations down the sampling tube) filtering according to Massman (2000), using a site-specific cospectral reference model (Wohlfahrt et al., 2005a). The high pass, non-recursive, finite impulse response (FIR) filter was applied digitally to account for an overestimation of the flux contributions of low-frequency eddies, using a Hamming window with time constants of 50 and 100 s for final, best guess CH₄ and N₂O fluxes, respectively. This procedure filtered out unwanted flux contributions at frequencies < 0.05 Hz, missing low-frequencies were then back-corrected based on the site-specific reference model co-spectrum (Wohlfahrt et al., 2005b).

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Two days in April 2011 are used to exemplify the effect of different FIR filters, applied to the CH₄ and N₂O time series, on the resulting flux estimates (Fig. 1b). The largest difference between unfiltered and filtered data as well as between the different filter time constants was found during night time. In contrast, during turbulent conditions e.g. around noon, fluxes calculated with different time constants exhibited exchange patterns of comparable magnitude (Fig. 1b, left panels). FIR filtering had a larger effect on CH₄ than on N₂O fluxes. As an example, over the course of one day unfiltered CH₄ exchange rates fluctuated between -13.5 and 48.6 nmol m⁻² s⁻¹ (average: 0.24 ± 16.18 nmol m⁻² s⁻¹), while best guess fluxes ranged between -6.0 and 5.4 nmol m⁻² s⁻¹ after FIR filtering (-0.42 ± 3.16). Similarly, unfiltered N₂O fluxes were between -0.87 – 3.32 nmol m⁻² s⁻¹ (0.24 ± 1.05), with best guess fluxes of -0.74 – 0.40 nmol m⁻² s⁻¹ (-0.12 ± 0.35). Cospectral analyses revealed that lower frequencies of the CH₄ and N₂O fluxes were overrepresented compared to the sensible heat flux (Fig. 1b, right panels).

In total, 28 891 flux values were calculated for CH₄/N₂O. Flux results of each FIR run required separate quality control. When applying a FIR filter with a time constant of 50 s/100 s/150 s to the data, 57/55/55 % of all CH₄ fluxes and 66/64/63 % of all N₂O fluxes passed all quality tests, respectively. However, only 28 % and 39 % of all CH₄ and N₂O fluxes, respectively, passed all tests when no FIR filter was used in the flux calculations. Only data that passed all quality tests in a respective scenario were used in the present study.

Instrumentation, data treatment and quality control of CO₂, sensible and latent heat fluxes have been described at length by Wohlfahrt et al. (2008) and Hammerle et al. (2008).

2.6 Quality control

Half-hourly methane and nitrous oxide fluxes were excluded from the analysis if (i) the deviation of the integral similarity characteristics was larger than 60 % (Foken and

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Wichura, 1996), (ii) the maximum of the footprint function (Hsieh et al., 2000) was outside the boundaries of the meadow, (iii) fluxes were outside a specific range (CH₄: $\pm 50 \text{ nmol m}^{-2} \text{ s}^{-1}$, N₂O: $\pm 5 \text{ nmol m}^{-2} \text{ s}^{-1}$), (iv) half-hourly VMRs were outside a specific range (CH₄: 1800–3500 ppb, N₂O: 280–450 ppb), (v) the stationarity test for the
5 respective flux exceeded 60 % (Foken and Wichura, 1996), (vi) the third rotation angle exceeded 10° (McMillen, 1988), (vii) the number of half-hourly VMR values was below 3000 or (viii) more than 20 % of data were classified as spikes in any half-hourly period.

2.7 Ancillary data

Major environmental parameters were measured continuously at the field site, including air temperature (T_{air}), soil temperature (T_{soil}) at 0.05 m depth (TCAV thermocouple, Campbell Scientific, Logan, UT, USA), volumetric soil water content (SWC) (ML2x, Delta-T Devices, Cambridge, UK), soil heat flux (SHF) quantified by means of heat flux plates (3 replicates at 0.05 m depth, corrected for the change in heat storage above that depth; HFP01, Hukseflux, Delft, the Netherlands), total photosynthetically active radiation (PAR) (BF3H, Delta-T, Cambridge, UK) and precipitation (52202, R. M. Young, Traverse City, MI, USA). All data were collected continuously by a data logger (CR10X, Campbell Scientific, Logan, UT, USA). The green plant area index (GAI) was assessed
15 (i) in a destructive fashion by harvesting the plant matter of square plots (0.09 m², 3–5 replicates) and subsequent plant area determination (Li-3100, LiCor, Lincoln, NE, USA) and (ii) from measurements of canopy height which was related to destructively measured GAI (Wohlfahrt et al., 2008b). Continuous time series of the GAI were derived by fitting appropriate empirical functions to measured data separately for each growing phase before and after cutting events. A more detailed list of all auxiliary parameters measured at this site is given by Wohlfahrt et al. (2008b) and Hammerle et al. (2008).
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2.8 Statistical analyses

Statistical analyses were done using *Statistica 9* (StatSoft, Inc.), *SigmaPlot 12.5* (Systat Software, Inc.) and *Excel 2010* (Microsoft, Inc.). The *partial correlation* in the multiple linear regression analysis gives the correlation between two variables after controlling for the effect of all other variables in the equation. To determine significant differences between group means in a repeated measures analysis of variance (ANOVA) setting, the Unequal N HSD post hoc test, a modification of the Tukey's HSD test, was used. For statistical analyses, only days or half-hours where all parameters were available were included. In case of ancillary data, the daily average of the respective parameter was calculated when at least 40 half-hours of data were present for the respective day. In comparison, fewer values were available for CH₄/N₂O fluxes and VMRs due to the strict quality criteria. For CH₄/N₂O data, the daily average was regarded as representative for the day when at least 14 half-hours were available after quality control. In total 91 and 95 % of the presented CH₄ and N₂O daily average values, respectively, were calculated from at least 20 half-hourly values.

3 Results

Daily average values of CH₄/N₂O fluxes were calculated for 567/574 out of 684 days, respectively (Fig. 2). While fluxes of both compounds fluctuated around zero towards the end of the vegetation period and during snow cover, net emission and deposition on a daily basis occurred for both compounds during certain time periods. Daily net uptake (negative sign) was recorded on 162/203 days, whereby time periods characterized by clear deposition were found especially for N₂O, for example some weeks after snowmelt in spring 2011 (Fig. 2). Highest daily average emissions for both compounds were found around the 2nd cutting of the meadow at the end of July 2010 (7.7/0.76 nmol m⁻² s⁻¹). CH₄ VMRs were highest during snow cover and lowest during periods of strong growth (Fig. 2). We attribute the sudden drop of N₂O concentration

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values around the 1st cut in 2010 to a problem with the zero-calibration of the QCL. Over all two years, the median VMR was 2.02/0.32 ppm for CH₄/N₂O, respectively, the median flux amounted to 0.60/0.02 nmol m⁻² s⁻¹ (Fig. 2).

Daily average PAR was found between approx. 40 μmol m⁻² s⁻¹ in winter and 674 μmol m⁻² s⁻¹ in summer, with a median value of 215 μmol m⁻² s⁻¹. In 2010, the yearly average T_{air} at the field site of 6.1 °C was colder than the long term average (2001–2007) of 6.7 °C, while 2011 was warmer than average (7.1 °C). During this study, the maximum daily average T_{air} was 22.7 °C in July 2010, the minimum of –17.3 °C was recorded in February 2012 (Fig. 2). T_{soil} was similar in both years, about 8.5 °C on average and values just above 0 °C when snow covered the ground. SWC was highest immediately after snow melt, with a maximum daily average value of 0.44 m³ m⁻³ at the end of February 2010, and lowest in May 2011 after a period of only little precipitation (0.08 m³ m⁻³). In 2011, SWC was generally low (0.25 m³ m⁻³ averaged over the growing season) and significantly lower ($p < 0.001$) than in 2010 (0.32 m³ m⁻³). Over the duration of the flux measurements, precipitation was detected on 262 days, amounting to 525 and 537 mm in 2010 and 2011, respectively, and 46 mm over the first two months in 2012 (Fig. 2). Relative air humidity (RHA) was around 80 % on average over the whole measurement campaign, with minima below 50 % in June 2010 (Fig. 2). In 2010 and 2011, highest VPD values of more than 1 kPa were recorded during the warmer months between the end of May and August. GAI was below 1 m² m⁻² right after snow melt, reached maximum values of up to 8 m² m⁻² right before the 1st cut and was then reduced to below 1.5 m² m⁻² as a consequence of the cutting. GAI maxima before the 2nd and 3rd cut were lower compared to the 1st cut. Towards the end of the year after the 3rd cut, GAI first increased and later decreased due to vegetation regrowth and senescence, respectively (Fig. 2).

The meadow was a source for CO₂ during snow cover and became a net sink for CO₂ some weeks after snowmelt and until the 1st cut (Fig. 3). The cutting event turned the meadow into a CO₂ source for about two weeks before it again became a net sink. This behavior recurred after the 2nd and 3rd cut, however the CO₂ uptake after the last

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cutting was less pronounced than after the previous cuttings. More information about CO₂ fluxes at the site was given by Wohlfahrt et al. (2008).

Fluxes of both CH₄ and N₂O showed high variability on a half-hourly time scale, especially during the first two months of the measurements and during the night (Fig. 3). However, 95 % of all half-hourly CH₄ fluxes during the vegetation period were found between $\pm 10 \text{ nmol m}^{-2} \text{ s}^{-1}$ and 96 % of all N₂O fluxes between $\pm 1 \text{ nmol m}^{-2} \text{ s}^{-1}$. During snow-free conditions and including only days not influenced by management events, the average CH₄/N₂O flux was found at $0.87 \pm 5.03/0.06 \pm 0.49 \text{ nmol m}^{-2} \text{ s}^{-1}$, respectively (Fig. 3). Compared to these undisturbed conditions, average fluxes were higher on days where the meadow was influenced by cutting events ($1.09 \pm 5.22/0.11 \pm 0.47 \text{ nmol m}^{-2} \text{ s}^{-1}$) and lower on days characterized by snow cover ($0.13 \pm 5.16/0.02 \pm 0.47$). The day of manure spreading and the two days thereafter were covered by our measurements only in October 2011. On the day of fertilization and two days later, average N₂O fluxes were elevated ($0.08 \pm 0.39 \text{ nmol m}^{-2} \text{ s}^{-1}$) when compared to the rest of the same month (0.04 ± 0.31), while CH₄ fluxes remained virtually unaffected (1.54 ± 5.67 vs. 1.68 ± 5.54). In total, emission fluxes were observed in 56/57 % of all recorded CH₄/N₂O half hour periods (Fig. 3).

Average diurnal cycles of CH₄ and N₂O were often characterized by high variability with large fluctuations around zero, but followed a clear diurnal cycle during certain time periods (Fig. 4). Methane fluxes showed weak diurnal cycles after snowmelt and before the 2nd cut in 2011, with peak average uptake rates of $-1.93 \text{ nmol m}^{-2} \text{ s}^{-1}$ around noon. The clear uptake of CH₄ before the 1st cut coincided with strong N₂O deposition during daytime, with average peak rates of up to $-0.28 \text{ nmol m}^{-2} \text{ s}^{-1}$ in the early afternoon. While CH₄ fluxes continued to exhibit a very similar deposition pattern up until the 2nd cut, N₂O fluxes switched in sign and showed a clear diurnal cycle of constant emission during daytime, up to $0.35 \text{ nmol m}^{-2} \text{ s}^{-1}$ on average just before noon. The N₂O flux pattern after the 1st and before the 2nd cut was very similar in both years, whereby peak emission rates in 2010 occurred earlier in the day (Fig. 4). In contrast to CH₄ fluxes, which showed no clear diurnal pattern after the 2nd cut in

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both years, the meadow constantly emitted N_2O during daytime and before the 3rd cut in 2011, on average up to $0.61 \text{ nmol m}^{-2} \text{ s}^{-1}$ around noon, while during daytime after the 3rd cut in 2010 N_2O was transported to the meadow, peak deposition amounted to $-0.17 \text{ nmol m}^{-2} \text{ s}^{-1}$ on average. During snow cover, fluxes of both compounds fluctuated around zero (Fig. 4).

When all data were pooled, a multiple linear regression (MLR) analysis explained 26/38 % of the variability in daily average $\text{CH}_4/\text{N}_2\text{O}$ fluxes (Table 1). Over all years, the partial correlation (PC) of the net ecosystem exchange of CO_2 (NEE) with methane fluxes was high and positive in sign, while SHF was negatively correlated with CH_4 exchange; both PCs were highly significant ($p < 0.001$). During shorter time periods in-between, before and after cutting events in single years the chosen set of parameters explained between 23 and 62 % of the observed flux variability, with r^2 being highly significant only once, namely in a period of high CH_4 uptake before the 1st cut 2011, with NEE and H as the dominant regressors (Table 1). Explaining the CH_4 flux variance during the same time periods but using data of both years worked best during the vegetation period until the 2nd cut, and again after the 3rd cut until snow cover, explaining up to 39 % of observed CH_4 fluxes. SHF and NEE both featured significant PCs in the first half of the year up until the 2nd cut, with NEE remaining a significant regressor after the 3rd cut. LE showed a high PC towards the end of the vegetation period and during snow cover (Table 1). A simple linear regression (SLR) analysis using all data lead to results similar to those of the MLR, with highly significant and positive correlations found for T_{air} , T_{soil} and NEE, and a negative correlation for CH_4 VMR (Table 1).

Generally, the MLR analysis resulted in r^2 being considerably higher for N_2O than for CH_4 fluxes (Table 1). The PCs were highly significant for multiple regressors. A positive PC of similar magnitude was found for the ecosystem fluxes NEE and LE, and in addition for RHA and N_2O VMR. Negative PCs were most prominently found for SWC and H . The regressors were able to explain between 56 and 75 % of the N_2O flux variance during shorter time periods in single years, with the exception of the time period

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before the 1st cut 2010 when r^2 was found to be statistically not significant (Table 1). The chosen set of parameters performed well with pooled data during the same time periods and especially after the 1st cut, explaining between 66 and 73 % of observed daily average N₂O fluxes. SWC was the most dominant regressor towards the end of the year, featuring a highly significant, negative PC (Table 1). Similarly, T_{soil} was an important parameter in the MLR analysis after the 1st cut, being first positively, later negatively correlated with N₂O exchange. In a simple linear regression nine out of 11 parameters were significantly correlated with the N₂O flux, with T_{air} and T_{soil} as the highest positively and SWC as the highest negatively correlated regressors, respectively (Table 1). A closer look at the two most prominent soil related regressors, T_{soil} and SWC, and the N₂O flux under snow-free, undisturbed conditions revealed a clear pattern. Daily average N₂O exchange showed a bell-shaped relationship with SWC with highest emissions during periods of intermediate soil water content (Fig. 5, top panel). Even clearer was the correlation between T_{soil} and N₂O flux: days with a daily average T_{soil} above 14 °C showed an almost consistent net emission of N₂O. This was also observed for days where T_{soil} was close to zero, whereas N₂O exchange fluctuated around zero with no clear pattern between 0 and 14 °C (Fig. 5, middle panel). Taking both SWC and T_{soil} into account, days characterized by low to intermediate SWC with T_{soil} close to 0 °C or above 14 °C generally resulted in a net emission of N₂O, while deposition was mainly observed during cool conditions with high SWC (Fig. 5, lower panel). In contrast to N₂O, comparably clear exchange patterns were not found for CH₄ fluxes.

On a daily average time scale, a repeated measures ANOVA revealed statistically significant differences among environmental conditions on days with net uptake (group f⁻), net emission (f⁺) or close-to-zero exchange (f⁰) of CH₄ and N₂O (Table 2). In case of CH₄, T_{air} was significantly colder on low-flux days than on emission and deposition days. Generally, environmental conditions were most different between high deposition days and days resulting in emission or close-to-zero exchange of CH₄ (Table 2). In group f⁻, the ecosystem fluxes LE and H, SHF, PAR, VPD and RHA were all sig-

nificantly higher compared to f+ and f0, while also the net uptake of CO₂ was larger. Although results were less clear for N₂O fluxes, the meadow tended to act neither as a source or sink on days when air and soil temperatures as well as LE were low (Table 2). In addition, SWC was significantly lower in f+, while H was significantly higher on deposition days.

Cumulative fluxes for 2011 resulted in a net CO₂-uptake of -70.5 g CO₂ m⁻² (Fig. 6). CH₄ and N₂O fluxes were converted to CO₂-equivalents, with cumulative fluxes being calculated for each of the different FIR filter time constants. In 2011, the meadow acted as a source for both compounds. When no FIR filter was applied, i.e. the overestimation of the low frequency eddy flux contribution was not corrected for, cumulative methane fluxes amounted to an emission of 54.5 g CO₂-equ. m⁻². With FIR filters of varying time constants, cumulative fluxes were considerably lower, in the range of 6.8–19.3 g CO₂-equ. m⁻², whereby the lower number was obtained using a FIR filter time constant of 50 s and constitutes the best guess estimate. Results were very similar for N₂O, the cumulative fluxes of which resulted in a net emission of 97.9 g CO₂-equ. m⁻² without FIR filter, and 25.2–39.8 g CO₂-equ. m⁻² using filters with different time constants. In case of N₂O, a time constant of 100 s was considered to give the most representative flux results, yielding 32.0 g CO₂-equ. m⁻² over the whole year (Fig. 6).

The total GHG budget can be calculated by summing up the different cumulative contributions of CO₂, CH₄ and N₂O. Based on the best guess estimates, the meadow acted as a GHG sink (-31.7 g CO₂-equ. m⁻²) in 2011. However, when no FIR filter was applied to neither CH₄ nor N₂O data, the sum of the two compound fluxes more than compensated for the sink effect of CO₂, turning the meadow into a GHG source (81.9 g CO₂-equ. m⁻²; Fig. 6).

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4 Discussion

4.1 Methane

It was shown recently that plants do not contain a known biochemical pathway to synthesize methane (Nisbet et al., 2009), a finding that contradicts observations of methane emissions from terrestrial plants under aerobic conditions in an earlier study (Keppler et al., 2006). Methane emissions from plant tissue may be due to the transpiration of water that contains dissolved CH₄ or due to the abiotic breakdown of plant material as a consequence of high UV stress conditions (Nisbet et al., 2009), but the contribution of terrestrial plants to the global methane emission is considered to be small (Dueck et al., 2007). Based on these earlier findings it is feasible to regard observed eddy covariance emission fluxes in this study as a direct (methanogen microorganisms) or indirect (transpiration of soil CH₄) consequence of processes in the soil, an important player in the global methane cycle (Kirschke et al., 2013; Smith et al., 2000).

Therefore, one might expect clear relationships between soil environmental parameters such as temperature or moisture and CH₄ exchange, which were also reported by other studies (Dijkstra et al., 2013; Hartmann et al., 2010; Imer et al., 2013; Jackowicz-Korczyński et al., 2010; Liebig et al., 2009; Rinne et al., 2007; Schrier-Uijl et al., 2010). However, when all data were pooled no clear correlation between soil parameters and eddy covariance CH₄ exchange at the grassland site in Neustift was observed. Although the explanatory power of T_{soil} in the MLR was relatively high and significant between the 1st and 2nd cutting of the meadow in 2011 – a period when small quantities of CH₄ were taken up by the meadow around noon – no consistent relationship between soil parameters and the CH₄ flux was observed (Table 1). SHF was significantly higher on days with net deposition compared to zero-flux and net emission days (Table 2) and might be an indication of soil processes as possible drivers for observed exchange patterns. The partial correlations of SWC with CH₄ exchange, however, were statistically not significant throughout the measurement campaign and virtually zero

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when all data were pooled (Table 2). This is in contrast to chamber studies that identified soil moisture as a key driver for methane exchange (e.g. Dijkstra et al., 2013b).

One explanation for this lack of correlation between soil parameters and methane fluxes might be that half-hourly eddy covariance fluxes represent an integral signal, averaged over 30 min over a possibly heterogeneous area of methane sources and covering both “hot spots” of high methane emission and areas of relatively high uptake within the same flux footprint (Baldocchi et al., 2012). Therefore, SWC may be high in certain patches of the meadow and create environmental conditions conducive for methanogenic microorganisms, but low in other microsites across the grassland. Half-hourly fluxes reflect this heterogeneity across the footprint to a varying degree, mainly depending on wind direction, wind speed and atmospheric stability. In addition, the direct effect of certain drivers on CH₄ exchange may smear out at ecosystem scale. Recently Yvon-Durocher et al. (2014) found an average temperature dependence of CH₄ emissions from aquatic, wetland and rice-paddy ecosystems similar to that of CH₄ production derived from pure cultures of methanogens and anaerobic microbial communities in the laboratory. No such relationship was found in the present study, which may be a direct consequence of a heterogeneous footprint with regards to CH₄ sources and generally low CH₄ fluxes at the measurement site in Neustift.

The observation of weak CH₄ uptake around noon between March and July 2011 (Fig. 2) is most likely a consequence of methanotrophic microorganisms in the soil, a process enhanced by increased soil temperature. However, it is difficult to observe this temperature dependence at ecosystem scale, as the whole footprint regardless of emission/deposition hot spots is sampled. In addition, it was shown that both methanotrophic and methanogenic activity in the soil are temperature dependent (von Fischer and Hedin, 2007; Yavitt et al., 1995), whereby the latter tends to be more responsive to temperature (Topp and Pattey, 1997). Imer et al. (2013) reported nearly consistent methane uptake throughout the year except for winter at three different grassland sites along an altitudinal and management gradient using static chambers, with flux rates

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of generally below $1 \text{ nmol m}^{-2} \text{ s}^{-1}$. Three pastures investigated by Liebig et al. (2009) were identified as minor CH_4 sinks.

Daily average CH_4 emissions in this study generally ranged between $0\text{--}5 \text{ nmol m}^{-2} \text{ s}^{-1}$ and were relatively similar to eddy covariance results over a drained and grazed peatland pasture during dry periods, when fluxes were often below $10 \text{ nmol m}^{-2} \text{ s}^{-1}$ (Fig. 2; Baldocchi et al., 2012). However, the maximum CH_4 flux and concentration of around $360 \text{ nmol m}^{-2} \text{ s}^{-1}$ and 3500 ppb , respectively, at the peatland site were much higher than the $8 \text{ nmol m}^{-2} \text{ s}^{-1}$ and 2300 ppb recorded at Neustift. Higher maximum methane fluxes were also observed by Schrier-Uijl et al. (2010) over a grass ecosystem on peat ($100 \text{ nmol m}^{-2} \text{ s}^{-1}$).

In comparison to CO_2 and energy fluxes, there are only few long-term EC methane exchange studies. However, year-round measurements are indispensable for accurately estimating the CH_4 budget of an ecosystem. Baldocchi et al. (2012) give a three-year mean annual methane efflux at a peatland pasture of $8.7 \pm 6.7 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ without any discrimination for cattle or elongated footprints during the night, and $2.7 \pm 1.4 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ when only daytime data representing the well-drained portion of the pasture, additionally filtered for favorable wind directions and the presence of cows, were used. This latter number is relatively similar to the methane efflux of $1.6 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ in Neustift in 2011. In comparison, Hendriks et al. (2007) reported $10.6 \pm 19.5 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ from the relatively dry portions of an abandoned peat meadow using chamber measurements, and $31.8 \pm 20.7 \text{ g CH}_4\text{-C m}^{-2} \text{ yr}^{-1}$ when the whole meadow, including water-saturated land and ditches, was considered. Mander et al. (2010) conducted a literature survey and reported median fluxes of $1.2 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$ for fertilized grasslands on hydromorphic soils in Estonia, similar to Neustift ($2.0 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$). Methane emissions reported by Merbold et al. (2014) from a grassland after restoration where one order of magnitude higher ($27 \text{ kg CH}_4\text{-C ha}^{-1} \text{ yr}^{-1}$). Using eddy covariance measurements, methane emissions

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between 18–22 g CH₄-C m⁻² yr⁻¹ were reported from a subarctic peatland (Jackowicz-Korczyński et al., 2010) and 9.4 g CH₄-C m⁻² yr⁻¹ from a boreal fen (Rinne et al., 2007).

Baldocchi et al. (2012) reported mean diurnal patterns characterized by lowest methane efflux densities during midday and elevated methane emission throughout the night, a pattern very similar to Neustift during certain time periods, e.g. between the 1st–2nd cut 2010 (Fig. 4). We mainly attributed this observation to meteorological factors, i.e. intermittent exchange during calm and stable nighttime conditions, which was also the reasoning behind the outlier handling in our despiking procedure (Fig. 1a). Another reason might be the preferential sampling of an elevated methane source in combination with a larger nighttime footprint as described by Baldocchi et al. (2012). It is possible that methane emissions from a small stream and adjacent wet patches of the meadow, that are normally not part of the footprint, have contributed disproportionately to observed methane emissions.

Several studies reported that 81–90 % of the total annual methane emission occurred during the snow free period or between spring – autumn (Jackowicz-Korczyński et al., 2010; Rinne et al., 2007), which is very similar to Neustift in 2011, where 84 % of the yearly net CH₄ emission occurred during snow free conditions.

4.2 Nitrous oxide

Despite occasional uptake, the meadow was a source of N₂O, in accordance with previous studies over managed grasslands. Half-hourly emission rates of N₂O, mostly below 1 nmol m⁻² s⁻¹, were similar to exchange rates reported by Neftel et al. (2010) for an experimental farm site and Imer et al. (2013) from a mountain rangeland. N₂O fluxes in 2011 amounted to an emission of 0.7 kg N₂O-N ha⁻¹ yr⁻¹. For comparison, Mander et al. (2010) reported approx. 0.6 and 4.6 kg N₂O-N ha⁻¹ yr⁻¹ for unfertilized and fertilized grasslands, respectively. Merbold et al. (2014) observed 29 kg N₂O-N ha⁻¹ yr⁻¹ for a grassland after restoration.

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Many of the observations made for CH₄ were also valid for N₂O, with generally low fluxes, a possibly heterogeneous flux footprint with respect to emission/deposition hot spots and soil processes as the driving force behind N₂O exchange patterns. In contrast to CH₄ exchange, N₂O fluxes on a daily scale could be well explained by environmental parameters during specific time periods. The important role of temperature in soil processes was shown previously, as N mineralization, nitrification, denitrification and N₂O emissions all increase with temperature (Barnard et al., 2005), while reduced soil moisture as a result of high air temperatures and increased plant transpiration can decrease N₂O emissions (Li et al., 1992). These findings are comparable to observations in the present study, where N₂O exchange tended to emission during warm and relatively dry soil conditions (Fig. 5, lower panel).

N₂O consumption in the soil occurs when N₂O reduction exceeds N₂O production (Chapuis-Lardy et al., 2007). Soil water is probably the key driver regulating N₂O consumption in soils, as it can act as a temporary storage body that entraps N₂O, effectively hindering its diffusion from the soil matrix to the surface. As a consequence, the time for potential reduction of N₂O to N₂ through anaerobic denitrification is increased (Clough et al., 2005). This can result in a low N₂O/N₂ ratio during wet conditions, which favors N₂O consumption (Ruser et al., 2006; Wu et al., 2013). These observations agree with our findings at ecosystem scale. When all data were pooled, N₂O uptake was highest during relatively wet conditions (Fig. 5, top panel). In addition, SWC was significantly lower on days with clear net emission of N₂O (Table 2).

In October 2011, manure application resulted in a pulse of N₂O emission one day later, after which fluxes rapidly decreased and reached pre-fertilization rates two days after manure spreading. Similar behavior of N₂O fluxes returning to background levels within 2–6 days after fertilization has been observed by Jones et al. (2011) for a Scottish grassland and Neftel et al. (2010) for an experimental farm site. Pulses of N₂O emissions after fertilizer application were also described in other studies (e.g. Granli and Bockman, 1994; Jones et al., 2011) and might be the result of animal manure – the most concentrated form of anthropogenic N input (Davidson, 2009) – directly fueling

nitrifying and denitrifying bacteria in the soil, which are most active when N is abundant (Firestone and Davidson, 1989). Over the weeks following fertilization, N₂O emissions increased with air temperature, which is in-line with the temperature dependence of the involved processes. We observed a sharp increase of N₂O emissions once the daily average air temperature fell below the freezing point, approx. four weeks after manure spreading in November 2011. During this time period the meadow remained snow-free, with soil temperatures close to 0 °C. The combination of reduced plant metabolism (low nitrate demand by plants) and prior manure spreading could result in an abundance of soil NO₃⁻ at the end of the vegetation period. Wertz et al. (2013) showed that denitrification can still occur at very low temperatures and even below the freezing point when NO₃⁻ and C are present. The observation of high N₂O emissions from frozen or nearly frozen soil was also made by earlier studies (Röver et al., 1998; Teepe et al., 2001).

Production and subsequent emission of N₂O remained high after the beginning of the snow cover in December 2011. Zhu et al. (2005) described a similar situation where microbial activity in the soil of a lowland tundra did not cease during snow cover and N₂O continuously diffused to the atmosphere through the snowpack. However, high N₂O emissions were not observed one year earlier during similar conditions.

4.3 Global warming potential

The availability of year-round data allows for the calculation of a yearly GWP balance over a specific ecosystem. Rinne et al. (2007) reported a GWP balance of +108 g CO₂-equ. m⁻² when taking into account CO₂ and CH₄ fluxes from a boreal fen, with respective fluxes amounting to -156 and +264 g CO₂-equ. m⁻². Although the respective balance was much lower in Neustift (-64 g CO₂-equ. m⁻²), the situation was similar in that the carbon uptake of the meadow through CO₂ was partially offset by carbon loss through CH₄ emission. The number in Neustift may change drastically on a year-to-year basis, as the meadow can act both as a source and sink of CO₂ (Wohlfahrt et al., 2008a), while it is supposedly a constant source of CH₄. Dijkstra et al. (2013)

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used static chambers to calculate the GWP for five years of CO₂ and CH₄ data in a semiarid grassland, ranging between -3 and -6 g CO₂-equ. m⁻². Liebig et al. (2009) investigated three years of CH₄/N₂O static chamber fluxes, soil organic carbon change, CO₂ emissions associated with N fertilizer production and CH₄ emission from enteric fermentation for three grazing management systems. The resulting net GWP between -78 – 40 g CO₂-equ. m⁻² yr⁻¹ is similar to -32 g CO₂-equ. m⁻² yr⁻¹ in this study when adding up CO₂, CH₄ and N₂O fluxes in 2011. Hendriks et al. (2007) reported -86 g CO₂-equ. m⁻² yr⁻¹ from an abandoned peat meadow. Merbold et al. (2014) give the full GHG flux budget of an intensively managed grassland after restoration, including ploughing. GHG emissions reported in their study were much higher than in Neustift, amounting to 2851 g CO₂-eq. m⁻². Zona et al. (2013) reported a GHG balance of -260 g CO₂-equ. m⁻² yr⁻¹ for a poplar plantation in 2011, taking into account CO₂ fluxes of -351 g CO₂-equ. m⁻² yr⁻¹, and CH₄ and N₂O fluxes of 49 and 42 g CO₂-equ. m⁻² yr⁻¹, respectively, with CH₄ and N₂O offsetting the NEE sink by 26 %. Soussana et al. (2007) investigated the GHG budget of nine European grassland sites over two years, covering a major climatic gradient and a wide range of management regimes. On average, the investigated grassland plots were a net sink of -240 g CO₂-C m⁻² yr⁻¹ for CO₂, and a net source of 32 and 14 g CO₂-C equ. m⁻² yr⁻¹ for CH₄ and N₂O, respectively, with emissions of the latter two compounds resulting in a 19 % offset of the NEE sink activity. In comparison, we found that the cumulative uptake of -19.2 g CO₂-C m⁻² yr⁻¹ in 2011 was offset by CH₄ and N₂O emissions of 1.9 and 8.7 g CO₂-C equ. m⁻² yr⁻¹, an offset of approx. 55 % of the NEE. Tian et al. (2014) reported offset ratios of 73 % for the whole North American continent, with the grassland GWP being nearly neutral.

5 Conclusion

The grassland site in Neustift is characterized by low fluxes of CH₄ and N₂O. In comparison to CO₂, H₂O and energy fluxes, the interpretation of CH₄ and N₂O exchange is challenging due to footprint heterogeneity, uncertainties regarding post-processing and quality control. Chamber measurements, concurrently performed with eddy covariance measurements, would provide more information about GHG producing and consuming patches within the flux footprint and allow for a more comprehensive interpretation of the bulk EC flux signal. Although the meadow can act as a source and sink for both compounds during certain time periods, it is a clear source of CH₄ and N₂O on an annual time scale. As a consequence, both gases contribute to an increase of the GWP, effectively reducing the sink strength of CO₂-equivalents at the investigated grassland site.

We conclude that CH₄ and N₂O fluxes over supposedly well-aerated and moderately fertilized soils cannot be neglected when evaluating the GHG impact of temperate managed grasslands. Both compounds can significantly influence the GWP balance of a meadow and be determining if a grassland is acting as a source or sink of CO₂-equivalents. In order to reliably assess GHG budgets on a local and global scale, long-term measurements of CH₄ and N₂O fluxes in combination with CO₂ exchange are necessary, especially over ecosystems that are normally characterized by low GHG fluxes.

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Table 1. Partial correlations of a multiple linear regression analysis and correlation coefficients (r) of a simple linear regression analysis using daily average values of air temperature (T_{air}), soil temperature (T_{soil}) and soil water content (SWC) in 5 cm depth, soil heat flux (SHF), net ecosystem CO₂ exchange (NEE), latent (LE) and sensible (H) heat flux, photosynthetically active radiation (PAR), vapor pressure deficit (VPD), relative air humidity (RHA) and CH₄/N₂O volume mixing ratios (VMR). Management events were excluded from the analysis. Bold numbers highlight $p < 0.05$, except bold underlined numbers resulted in $p < 0.001$.

	MULTIPLE LINEAR REGRESSION partial correlations												SIMPLE LINEAR REGRESSION r		
	all periods	snow melt–1st cut			1st cut–2nd cut			2nd cut–3rd cut			3rd cut–snow cover		snow cover	all periods	
	2010–2012	2010	2011	2010–2011	2010	2011	2010–2011	2010	2011	2010–2011	2010	2011	2010–2011	2010–2012	2010–2012
CH ₄ flux															
T_{air}	0.12	0.08	0.09	0.26	-0.09	-0.33	0.15	-0.04	0.32	-0.01	0.17	0.02	-0.03	0.16	0.28
T_{soil}	0.13	0.18	-0.10	-0.13	-0.12	0.57	0.08	-0.10	-0.12	-0.07	0.04	0.20	0.14	-0.11	0.27
SWC	0.04	0.05	-0.26	0.08	-0.29	-0.16	0.18	0.06	0.34	0.06	0.33	-0.08	-0.14	-0.14	0.01
SHF	-0.17	-0.16	-0.18	-0.27	0.16	0.22	-0.23	0.03	-0.27	0.03	-0.27	-0.11	-0.10	0.04	0.06
NEE	0.22	0.14	0.36	0.19	0.34	0.15	0.23	-0.10	0.04	-0.04	0.29	0.15	0.26	0.21	0.21
LE	-0.01	-0.08	-0.21	-0.11	0.15	-0.20	-0.04	-0.24	0.12	-0.18	0.23	0.44	0.43	0.32	-0.05
H	-0.12	-0.06	-0.39	-0.21	-0.31	-0.10	-0.10	-0.12	0.12	0.08	-0.04	-0.31	-0.21	-0.14	-0.07
PAR	0.05	0.19	0.20	0.26	-0.08	-0.09	0.06	0.29	-0.20	0.08	-0.15	-0.08	-0.12	0.03	0.00
VPD	-0.06	0.00	0.01	-0.14	-0.01	0.04	-0.05	0.21	-0.26	0.21	-0.09	-0.15	-0.06	-0.12	0.06
RHA	0.00	0.03	0.07	0.00	0.12	0.00	0.03	0.32	-0.28	0.24	-0.29	0.02	0.05	-0.06	0.09
CH ₄ VMR	0.03	0.16	-0.03	0.04	0.13	0.43	0.03	-0.40	0.11	-0.18	0.34	-0.15	-0.13	0.01	-0.17
multiple r^2	0.26	0.35	0.55	0.27	0.47	0.62	0.37	0.45	0.23	0.20	0.58	0.51	0.39	0.24	
N	438	47	67	114	50	36	86	44	40	84	35	37	72	82	458–542
N ₂ O flux															
T_{air}	0.11	-0.05	0.27	0.03	0.25	-0.01	0.05	0.12	0.15	0.22	0.03	0.05	0.04	0.16	0.31
T_{soil}	-0.05	0.09	-0.17	0.06	-0.16	0.20	0.28	-0.09	-0.07	-0.26	-0.22	-0.19	-0.32	-0.13	0.25
SWC	-0.24	-0.12	-0.16	-0.23	-0.18	-0.27	-0.20	-0.39	-0.29	-0.50	0.01	-0.45	-0.50	-0.07	-0.34
SHF	0.04	0.04	-0.23	0.23	-0.22	0.13	-0.11	-0.17	-0.13	-0.16	0.42	0.19	0.24	-0.10	0.19
NEE	0.21	-0.17	0.31	0.12	0.11	-0.06	0.11	0.35	0.24	0.32	0.32	-0.14	0.07	0.02	-0.04
LE	0.19	-0.13	-0.11	-0.07	-0.07	0.07	-0.02	0.03	0.20	0.11	0.40	0.04	0.16	0.19	0.24
H	-0.25	-0.25	-0.17	-0.23	-0.08	-0.23	-0.16	0.46	-0.01	0.19	0.21	-0.10	0.12	-0.25	-0.12
PAR	0.02	0.20	0.22	0.13	0.34	0.02	0.23	-0.19	0.18	0.03	-0.36	-0.03	-0.31	0.08	0.11
VPD	-0.02	-0.24	-0.11	-0.11	0.10	-0.08	0.11	0.23	0.04	0.21	-0.47	-0.05	-0.16	-0.10	0.20
RHA	0.23	-0.20	0.19	-0.02	0.44	0.00	0.31	0.34	0.23	0.35	-0.59	0.05	-0.12	0.01	0.03
N ₂ O VMR	0.25	-0.06	-0.09	0.03	0.37	0.26	0.25	-0.18	0.10	-0.14	-0.26	-0.07	-0.09	0.39	0.15
multiple r^2	0.38	0.19	0.56	0.25	0.75	0.73	0.66	0.72	0.56	0.67	0.73	0.69	0.73	0.44	
N	443	49	67	116	50	36	86	44	41	85	36	37	73	83	463–549

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Table 2. Daily average means in three different groups of daily net CH₄/N₂O exchange. Significant differences between group means were determined in a repeated measures ANOVA setting, using the Unequal N HSD post hoc test. Group labels to the right of a given group mean show to which flux group the respective value was significantly different. Bold numbers mark group means that were significantly different from one other group, except bold underlined numbers denote group means that were significantly different from both other groups. f+... daily average CH₄/N₂O emission fluxes > 0.2/0.01 nmol m⁻² s⁻¹, f0... fluxes between 0.2/0.01 and -0.2/-0.01 nmol m⁻² s⁻¹, f-... deposition fluxes < -0.2/-0.01 nmol m⁻² s⁻¹.

compound	Unit	Mean values and significant differences								
		CH ₄			N ₂ O					
flux class		f+	f-	f0	f+	f-	f0			
<i>T</i> _{air}	°C	9.2 f0	9.6 f0	5.9 f+, f-	10.1 f0	8.4 f0	4.2 f+, f-			
<i>T</i> _{soil}	°C	10.8	10.9	8.2	11.5 f0	10.1 f0	6.5 f+, f-			
SWC	m ³ m ⁻³	0.29	0.28	0.29	0.27 f-, f0	0.31 f+	0.32 f+			
SHF	W m ⁻²	1.0 f-	3.9 f+, f0	0.5 f-	2.2 f0	1.4	-1.5	f+		
NEE	μmol m ⁻² s ⁻¹	-1.6 f-	-5.0 f+	-2.7	-2.4	-3.2	-0.9			
LE	W m ⁻²	55.4 f-	85.9 f+, f0	50.2 f-	66.8 f0	63.6 f0	30.4 f+, f-			
<i>H</i>	W m ⁻²	6.9 f-	20.2 f+, f0	8.8 f-	7.5 f-	16.7 f+, f0	4.4 f-			
PAR	μmol m ⁻² s ⁻¹	270.5 f-	371.6 f+, f0	250.1 f-	293.3	314.0 f0	216.5 f-			
VPD	kPa	0.33 f-	0.42 f+, f0	0.28 f-	0.36	0.35	0.23			
RHA	%	80.8 f-	75.0 f+, f0	81.9 f-	80.7 f-	76.9 f+	81.5			
VMR	ppb	2013.7	2003.9	2020.5	318.8 f-	317.1 f+	318.6			
<i>N</i>	days	294	96	48	261	138	44			

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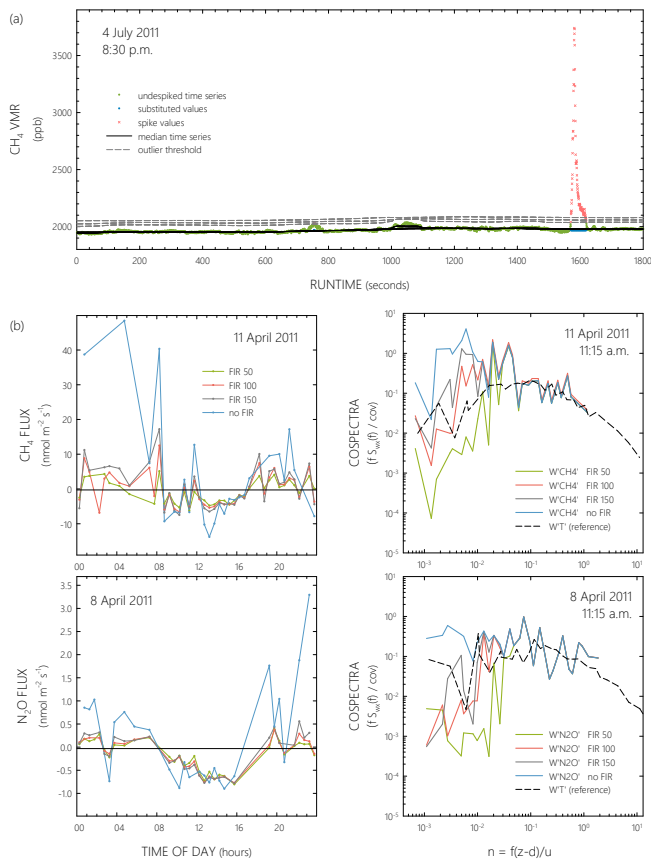


Figure 1. (a) Despiking example of 2 Hz methane VMRs using median filters. (b) Diurnal courses (left panels) and normalized co-spectra (right panels) illustrating the effect of high-pass filtering CH₄ (upper panels) and N₂O (lower panels) time series with a non-recursive finite impulse response (FIR) filter with different time constants (50, 100 und 150 s). Sensible heat cospectra are shown in the right panels for reference.

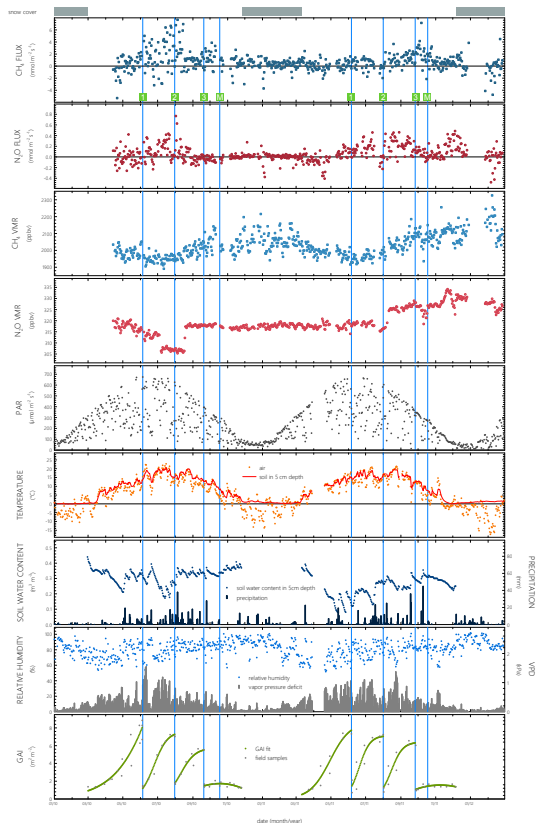


Figure 2. Daily average CH₄ and N₂O fluxes and volume mixing ratios (VMR), photosynthetically active radiation (PAR), air temperature, soil temperature at 5 cm depth, soil water content at 5 cm depth, relative air humidity, vapour pressure deficit, green plant area index (GAI) and daily sums of precipitation over 22 months of measurements between April 2010 and February 2012. Vertical lines show management dates, numbers 1, 2 and 3 in green squares indicate the 1st, 2nd and 3rd cutting of the meadow, respectively, while M denotes manure spreading.

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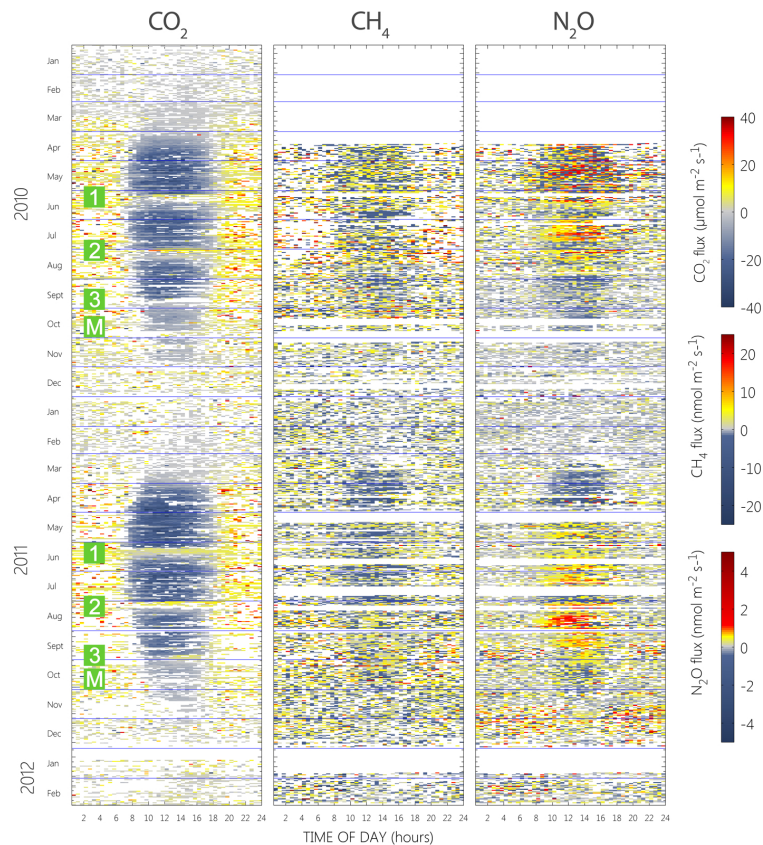


Figure 3. Half-hourly CO₂, CH₄ and N₂O fluxes over two years of GHG flux measurements. Numbers 1, 2 and 3 in green squares indicate the 1st, 2nd and 3rd cutting of the meadow, respectively, while M denotes manure spreading. Horizontal blue lines show the start and end of months. White color marks missing data.

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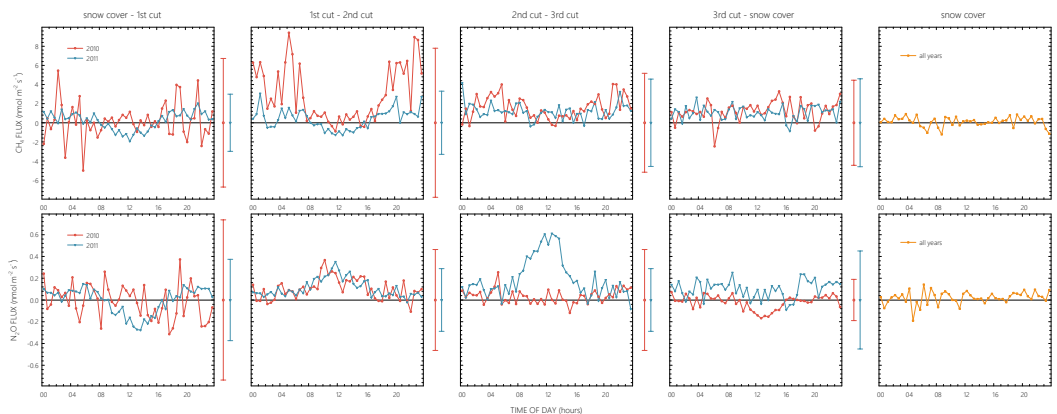


Figure 4. Diurnal cycles of CH₄ and N₂O fluxes during different time periods in 2010 and 2011. Whiskers to the right of each plot show the average standard deviation during the respective time period. Management data were excluded from the analysis.

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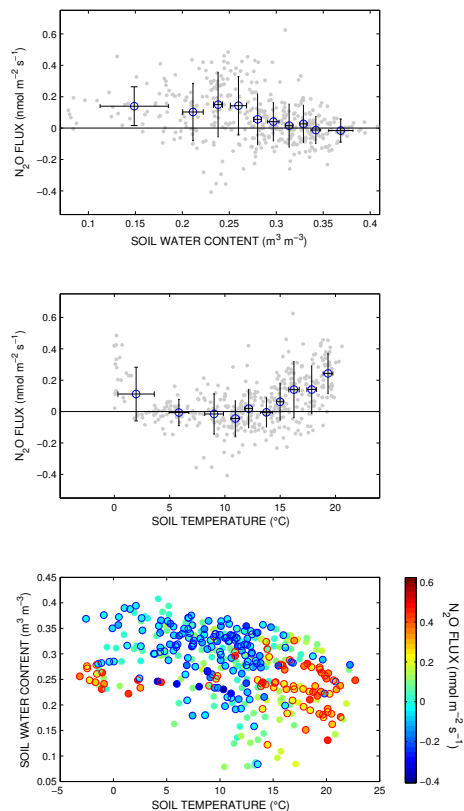


Figure 5. N₂O daily average fluxes (grey dots) vs. soil water content and soil temperature. Blue circles in the upper two panels show bin averages (40 days per bin), with error bars representing the standard deviation within each bin. In the lower panel, fluxes < 0 nmol m⁻² s⁻¹ are circled in blue, fluxes > 0.2 nmol m⁻² s⁻¹ are circled in red. Management events were excluded from the analysis.

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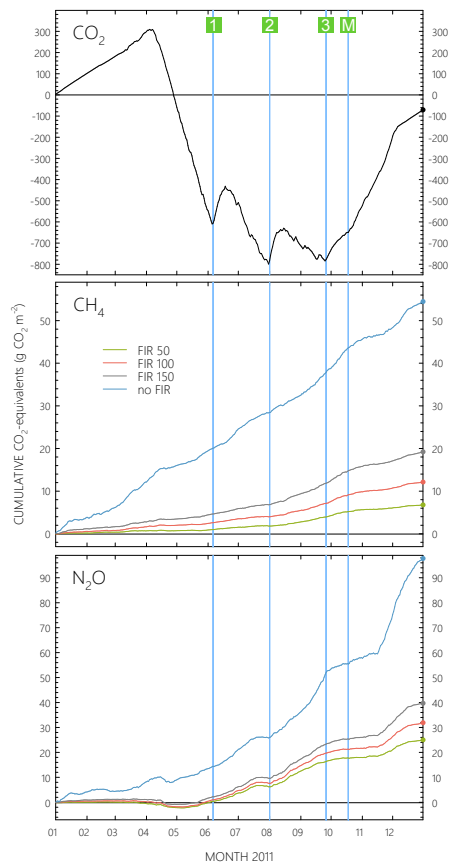


Figure 6. Cumulative GHG fluxes in 2011 expressed as CO₂-equivalents. The effect of the finite impulse response (FIR) filter with different time constants is shown for CH₄ and N₂O budgets. Vertical lines show management dates, numbers 1, 2 and 3 in green squares indicate the 1st, 2nd and 3rd cutting of the meadow, respectively, while M denotes manure spreading.